

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 706 455 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
27.08.2003 Bulletin 2003/35

(51) Int Cl.7: **B32B 31/00**

(86) International application number:
PCT/US94/07059

(21) Application number: **94921356.5**

(87) International publication number:
WO 95/000333 (05.01.1995 Gazette 1995/02)

(22) Date of filing: **22.06.1994****(54) IMPROVED STRUCTURES OF POLYMERS MADE FROM SINGLE SITE CATALYSTS**

MEHRSCICHTIGE STRUKTUREN AUS SINGLE-SITE KATALYSIERTEN POLYMEREN

STRUCTURES AMELIOREES DE POLYMERES PRODUITS A L'AIDE DE CATALYSEURS A SITE UNIQUE

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL
PT SE**

• **SEEKE, Gregory, J.**
Oshkosh, WI 54904 (US)

(30) Priority: **24.06.1993 US 82226**

(74) Representative: **MacGregor, Gordon et al**
Eric Potter Clarkson,
Park View House,
58 The Ropewalk
Nottingham NG1 5DD (GB)

(43) Date of publication of application:
17.04.1996 Bulletin 1996/16

(73) Proprietor: **AMERICAN NATIONAL CAN
COMPANY**
Chicago, Illinois 60631 (US)

(56) References cited:

EP-A- 0 170 385	EP-A- 0 451 977
EP-A- 0 461 848	EP-A- 0 516 019
EP-A- 0 552 911	EP-A- 0 597 502
WO-A-92/14784	WO-A-93/08221
WO-A-94/06857	WO-A-94/07954
WO-A-94/18263	US-A- 4 863 769
US-A- 4 871 705	US-A- 5 089 321
US-A- 5 206 075	

(72) Inventors:

- **ECKSTEIN, John, P.**
Neenah, WI 54956 (US)
- **ZHENG, Johnny, Q.**
Appleton, WI 54915 (US)
- **NORDNESS, Mark, E.**
Neenah, WI 54956 (US)
- **LIND, Keith, D.**
Appleton, WI 54911 (US)
- **WALBRUN, George, H.**
Menasha, WI 54952 (US)
- **SHEPARD, Mary, E.**
Oshkosh, WI 54901 (US)
- **JONES, Gregory, K.**
Appleton, WI 54914 (US)

- **PATENT ABSTRACTS OF JAPAN vol. 015, no.**
151 (M-1103), 16 April 1991 & JP-A-03 026541
(DAINIPPON PRINTING CO LTD), 5 February
1991,
- **ENCYCLOPEDIA OF POLYMER SCIENCE AND**
ENGINEERING, 1987, Volume 7, 'FILMS,
MANUFACTURE', pages 88-89.

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 706 455 B1

Description

BACKGROUND OF THE INVENTION

5 [0001] Polymeric materials have many applications in packaging structures. They are used as films, sheets, lidstock, pouches, tubes and bags. These polymeric materials may be employed as a single layer or one or more layers in a structure. Unfortunately, there are countless polymeric materials available. Furthermore, resin suppliers frequently have a tendency to claim many more applications for a product than the product is actually suitable for. In addition, in view of the specialized applications and processing problems that are encountered despite the suppliers claims, one skilled in the art can not tell whether a particular resin will be suitable for an application unless tested. However, for various reasons there are frequently drawbacks to the use of many of these polymeric materials. For example, ethylene vinyl alcohol is an excellent oxygen barrier material for use in packaging food products. However, this polymeric material can be affected by moisture that is present in the atmosphere or the packaged product. As a result, it is frequently found that some polymeric materials are better for certain applications than others.

15 [0002] One area where there is a need for suitable resins in film applications is in the area of heat shrinkable films. Heat shrinkable polymeric films are commonly used in packaging meats, particularly primal meat cuts and other large pieces of meat. While this description will detail the usage of films for packaging meat and meat by-products, it will be understood that these films are also suitable for packaging a myriad of other products, both including food products and non-food products.

20 [0003] Some of the films embodying the present invention are intended to be used by meat packers in the form of heat shrinkable bags with one opened end, which bags are closed and sealed after insertion of the meat. After the product is inserted, air is usually evacuated from the package and the open end of the bag is closed. Suitable methods of closing the bag include heat sealing, metal clips, adhesives etc. Heat is applied to the bag once sealing is completed to initiate shrinkage of the bag about the meat.

25 [0004] In subsequent processing of the meat, the bag may be opened and the meat removed for further cutting of the meat into user cuts, for example, for retail cuts or for institutional use.

[0005] Suitable shrink bags must satisfy a number of criteria. Many bag users seek a bag that is capable of surviving the physical process of filling, evacuating, sealing and heat shrinking. For example, during the shrinking process great stress can be placed on the film by the sharp edges of bone in the meat. The bag must also have sufficient strength to survive the material handling involved in moving the large cuts of meat, which may weigh a hundred pounds or more, along the distribution system.

[0006] Because many food products including meat deteriorate in the presence of oxygen and/or water, it is desirable that the bags have a barrier to prevent the infusion of deleterious gases and/or the loss or addition of moisture.

35 [0007] Conventional packaging for many products has frequently been made of multiple layer films having at least three layers. These multiple layer films are usually provided with at least one core layer of either an oxygen barrier material such as a vinylidene chloride copolymer, ethylene vinyl alcohol, a nylon or a metal foil preferably aluminum. Heat shrinkable meat bags, for example, have generally used vinylidene chloride copolymers. The copolymer of the vinylidene chloride may, for example, be a copolymer with vinyl chloride or methyl acrylate. Collapsible dispensing tubes have generally used one or more foil layers. The foil layers in addition to supplying an oxygen barrier also provide the dispensing tube with "deadfold", i.e., the property of a collapsible dispensing tube when squeezed to remain in the squeezed position without bouncing back.

40 [0008] Outer layers of films used in packaging food products can be any suitable polymeric material such as linear low density polyethylene, low density polyethylene, ionomers including sodium and zinc ionomers such ionomers include Surlyn, ethylene vinyl acetate etc. In conventional shrink bags, the outer layers are generally linear low density polyethylene or blends thereof. Suitable outer layers for meat bags are taught by U.S. Patent No. 4,457,960 to New-some.

[0009] WO 93/08221 and EP 0 516 019 teach substantially linear olefin polymers having improved processability. The polymers are formed using constrained geometry catalysts such as metallocenes.

50 [0010] The use of metallocene catalysts in the formation of olefin polymers is also disclosed in a number of other prior art documents. In particular, WO 92/14784 teaches heat sealable film structures for use in packaging wherein the heat sealable layer comprises a blend of very low density polyethylene with propylene based polymers.

[0011] EP 0 461 848 discloses ethylene/pentene-1 copolymers as packaging film material. The copolymers may be formed using a number of different polymerisation catalysts, which includes *inter alia* metallocene catalysts.

55 [0012] US 5,206,075 teaches laminar polyolefin film materials for packaging having a base film layer and a heat sealable film layer on one or both sides of the base layer. The heat sealable film layer comprises a very low density copolymer of ethylene and an alpha olefin comonomer formed in the presence of a metallocene catalyst.

[0013] While conventional films have been suitable for many applications, it has been found that there is a need for films that are stronger and more easily processed than conventional films. In meat bags, there is a need for films and

bags that have superior toughness and sealability and the ability to undergo cross-linking without undue deterioration. Thus, it is an object of the present invention to provide improved structures, including multi-layer films, sheets, lidstock pouches, tubes and bags. In particular, structures for use in shrink bags wherein the shrink bags are capable of withstanding production stresses and the shrink process.

SUMMARY OF THE INVENTION

[0014] The structures of the present invention are defined in claim 1. The structures may be multilayer films, sheets, lidstock, pouches, containers, tubes and bags where at least one layer contains a polymer usually a copolymer formed by a polymerization reaction in the presence of a single site catalyst such as a metallocene. Examples of such a polymer are ethylene and propylene polymers and copolymers thereof. One preferred copolymer is a copolymer of ethylene and an alpha olefin where such alpha olefin has a carbon chain length of from C₃-C₂₀. The structures of the present invention may also include blends of polymers and copolymers formed by a polymerization reaction with a single site catalyst or blends of a polymer and copolymer formed by a polymerization reaction with a single site catalyst and another polymeric material. Examples of suitable polymers for blending include: high and medium density polyethylene (HDPE, MDPE), linear low density polyethylene (LLDPE), low density polyethylene (LDPE), ethylene vinyl acetate (EVA), ultra low density polyethylene (ULDPE or VLDPE), and ionomers such as Surlyn. catalyst is a copolymer of ethylene and an alpha olefin such as octene-1. The structure of the present invention may be rendered oriented either uniaxially or biaxially and cross-linked by any suitable means, such as for example irradiation or chemical cross-linking.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

Figure 1 is a side view of a three layer structure outside of the present invention.

Figure 2 is a side view of a five layer film of the present invention.

Figures 3-6 are examples of the structure of metallocene catalysts used in the polymerization of the polymer used in the structures of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The structures of the present invention include films, sheets, lidstock, pouches, containers, tubes and bags. The structures are comprised of polymers that have been polymerized in the presence of a single site catalyst, such as a metallocene. A metallocene is a complex organometallic molecule typically containing zirconium or titanium, with a pair of cyclic alkyl molecules. More specifically, metallocene catalysts are usually compounds with two cyclopentadiene rings fixed to the metal. These catalysts are frequently used with aluminoxanes as a co-catalyst or an activator, one suitable aluminoxane is a methyl aluminoxane (MAO). Besides, titanium and zirconium, hafnium may also be used as the metal to which the cyclopentadiene is bonded. Alternative metallocenes may include Group IVA, VA and VIA transition metals with two cyclopentadiene rings. Also mono-cyclopentadiene rings or silyl amides may alternatively be in the metallocene instead of two cyclopentadienes. Other metals to which the cyclopentadiene may be attached may include the metals in the lanthanide series. Figures 3, 4, 5 and 6 show representative metallocenes that are suitable single site catalysts.

[0017] While the reaction mechanism is not completely understood, it is believed that the metallocene, single site catalyst confines the copolymerization reaction to a single site over the polymer thus controlling comonomer placement and side chain length and branching. The copolymers formed from metallocene single site catalysts are highly stereo regular products with narrow molecular weight distribution. The metallocenes can be used to polymerize ethylene, propylene, ethylenic and acetylenic monomers, dienes and carbon monoxide. Comonomers with ethylene and propylene include styrene, substituted styrene, vinyl, acrylonitrile, methyl acrylate, methyl methacrylate and 1,4 - hexadiene. The metallocene single site catalysts are capable of producing isotactic polymers and syndiotactic polymers, i.e., polymers in which the crystalline branches alternate regularly on both sides of the back bone of the polymer. There are two general types of single site catalyst reactions. The first are nonstereoselective catalysts reactions which have been developed by Exxon and Dow and which are used to make Exxon's Exact resins and Dow's CGCT resins. See Figs. 3 and 4. The second type of reactions are stereoselective catalysts developed by Hoechst and Fina for stereo specific polymerization particularly of polypropylene and other olefins such as butene-1, and 4 methylpentene-1. See, e.g., Figures 5 and 6.

[0018] The ethylene alpha olefins polymerized by a single site catalyst have low crystallinity and a density that ranges from 0.854 to 0.97 g/cm³. Although this density range is similar to conventional ethylene polymers, i.e., LDPE, LLDPE and ULDPE, the polymers in the structures of the present invention have a narrow molecular weight distribution and

homogeneous branching. The molecular weight distribution of the preferred polymers may be represented by the formula

$$\text{MWD} = M_w/M_n = <2.5$$

[0019] In addition, the melt processability of these polymers (I_{10}/I_2) has a range of about 5.5 to about 12 while conventional homogenous polymers are generally less than 6.5 at an MWD of 2. The melt tension of these polymers is in the range of about 1.5 to 3.5 grams.

[0020] The MWD of these polymers may be determined using a Waters 150 GPC at 140°C with linear columns (103₆ A-10⁶ Å) from Polymer Labs and a differential refractometer detector. Comparison of the MWD of a 1MI, 0.920 density CGCT polymer with that of 1MI, 0.920 density conventional LLDPE illustrates the very narrow MWD of the CGCT polymers which usually have a M_w/M_n of approximately 2 compared to 3 or greater for LLDPE.

[0021] A preferred ethylene copolymer is a copolymer of ethylene and a C₃ to C₂₀ alpha olefin. A preferred copolymer is a low modulus ethylene octene copolymer sold by Dow. This copolymer is formed by Dow's constrained-geometry catalyst technology which uses a single site catalyst such as cyclo-pentadienyl titanium complexes. As best understood, Dow's constrained geometry catalysts are based on group IV transition metals that are covalently bonded to a monocyclopentadienyl group bridged with a heteroatom. The bond angle between the monocyclopentadienyl group, the titanium center and the heteroatom is less than 115°. When the alpha olefin is present in the copolymer in the range of about 10 to 20% by weight these copolymers are referred to as plastomers. When the percent alpha olefin is greater than 20% these copolymers are called elastomers. The preferred ethylene octene copolymer has the octene comonomer present in an amount less than 25%. Examples of the Dow ethylene octene copolymer have the following physical properties.

DENSITY g/cm ³	MOLECULAR MELT WEIGHT DISTRIBUTION	MELT INDEX	MELT FLOW RATIO	STRENGTH
Polymer 1.				
0.920	1.97	1.0	9.5	1.89
0.910	1.90	1.0	7.9	1.68
0.902	2.10	1.0	7.6	1.68

Molecular weight distribution is defined as the ratio of weight average molecular weight to number average molecular weight. The lower the figure, the narrower the molecular weight distribution. Melt flow ratio is defined as the ratio of melt index, as tested with a 10-kg load to the melt index with a 2-kg load. The higher the ratio, the more processable the material. Melt flow ratio is defined as melt tension measured in grams. The higher the number the greater the melt strength. Other suitable resins are the Exact resins sold by Exxon, these resins have the following characteristics:

Typical properties of Exact medical grade polyethylenes						
Property	Value by grade					
	4028	4022	4021	4023	4024	4027
Melt index (D1238) ^a	10	6	22	35	3.8	4
Density, g/cm ³ (D-1505)	0.880	0.890	0.885	0.882	0.885	0.895
Hardness (D-2240)						
Shore A	78	84	84	80	83	89
Shore D	29	35	36	27	35	39
Tensile strength at break, Pa (p.s.i.) (D-638)	1.5×10 ⁷ (2220)	1.2×10 ⁷ (1700)	2.2×10 ⁷ (3260)	4.3×10 ⁶ (620)	2.0×10 ⁷ (2840)	1.5×10 ⁷ (2200)
Tensile elongation at break, % (D-638)	>800	>800	>800	>800	>800	>800
Tensile impact, N/m (ft.-lb./sq. in.) (D-1822)	3×10 ⁵ (145)	2.7×10 ⁵ (130)	7.4×10 ⁵ (350)	5.9×10 ⁵ (280)	6.3×10 ⁵ (300)	7.1×10 ⁵ (340)
Flexural modulus, Pa (p.s.i.) (D-790)	3.5×10 ⁷ (5040)	3.4×10 ⁷ (4930)	1.6×10 ⁷ (3980)	2.1×10 ⁷ (3100)	2.9×10 ⁷ (4180)	5.0×10 ⁷ (7230)

a:ASTM test method

(continued)

Typical properties of Exact medical grade polyethylenes						
	Value by grade					
Property	4028	4022	4021	4023	4024	4027
Vicat softening point °C (°F). (D-1525)	45 (138)	61 (168)	56 (158)	45 (138)	56 (158)	69 (181)

[0022] The structure of the present invention is comprised of an ethylene, propylene, or styrene polymer or copolymer formed by a polymerization reaction in the presence of a single site catalyst preferably a metallocene. Ethylene may be copolymerized with any suitable monomer such as $C_3 - C_{20}$ alpha olefin including propylene butene-1, 4-methyl pentene-1, hexene-1 and octene-1. A preferred comonomer is octene-1. The preferred ethylene alpha olefin copolymer of the present invention has a density in the range of .880 g/cm³ to about .920 g/cm³, a more preferred range of .890 g/cm³ to about .915 g/cm³ and a most preferred range of about .900 g/cm³ to about .912 g/cm³.

[0023] Figure 1 shows a cross section of a three layer coextruded structure outside of the present invention. Layer 14 is the core layer which may be a barrier layer that minimizes the transmission of oxygen through the structure. Preferred barrier materials are polyvinylidene chloride copolymers such as copolymers of vinylidene chloride and vinyl chloride or an alkyl acrylate such as methyl acrylate. Other preferred barrier material includes, ethylene vinyl alcohol, nylon or a metal foil such as aluminum. Layer 14 may also be a copolymer of ethylene and styrene formed using a single site catalyst in the polymerization reaction. The copolymer of vinylidene chloride may also be polymerized by the polymerization reaction in the presence of a single site catalyst. In addition, layer 14 may also be a polystyrene formed by a polymerization reaction in the presence of a single site catalyst. One such polystyrene is the crystalline syndiotactic polystyrene sold by Idemitsu Petro-Chemical Co., Tokyo, Japan.

[0024] On opposite sides of the core layer 14 of Figure 1 are layers 12 and 16. At least one of these layers 12 is a polymer formed by a polymerization reaction in the presence of a single site catalyst. The remaining layer 16 may be any suitable polymeric material such as a polyester, co-polyester, polyamide, polycarbonate, polypropylene, propylene-ethylene copolymer, ethylene-propylene copolymer, combinations of polypropylene and ethylene vinyl acetate copolymer, ultra low density polyethylene, low density polyethylene, medium density polyethylene, high density polyethylene, linear low density polyethylene copolymers; linear medium density polyethylene copolymer, linear high density polyethylene copolymer, ionomer, ethylene acrylic acid copolymer, ethylene ethyl acrylate copolymer, ethylene methyl acrylate copolymer, or ethylene methacrylic acid copolymer.

[0025] Alternatively, the layer 12 may be a blend of a polymer formed by a polymerization reaction in the presence of a single site catalyst and a suitable polymeric material such as is identified in connection with the description of layer 16 above.

[0026] In an embodiment of the invention, as shown in Figure 2, the five layer structure has a first layer 28 similar in composition to layer 12 of Figure 1, i.e., the film has a first layer of a polymer formed by the polymerization reaction with a single site catalyst or blends thereof with another suitable polymeric material. Both of the second 22 and fourth 26 layers are an adhesive layer.

[0027] The composition of adhesive layers 22 and 26 is selected for its capability to bond the core or barrier layer 24 to the surface layers 28 and 30. A variety of the well known extrudable adhesive polymers adhere well to the core or barrier layer 24. Thus, if for example layer 30 includes a polypropylene, an adhesive polymer based on polypropylene is desirably selected for layer 26. Examples of such adhesives are the extrudable polymers available under the trade designations Admer QF-500, QF550, or QF-551 from Mitsui Petrochemical Company, or Exxon 5610A2.

[0028] If the composition of layer 28 or 30 is an ethylene based polymer or copolymer, an adhesive polymer based on ethylene is preferably selected for layer 22, including ethylene homopolymer and copolymers. Such a preferred adhesive composition is an ethylene vinyl acetate copolymer containing 25% to 30% by weight vinyl acetate. Other ethylene based homopolymer and copolymers, modified to enhance adhesion properties are well known under the trade names of, for example, Bynel and Plexar. Typical base polymers for these extrudable adhesives are the polyethylene and the ethylene vinyl acetate copolymers. Such adhesive polymers, including the polypropylene-based polymers, are typically modified with carboxyl groups such as anhydride. Also acceptable as adhesives are ethylene methyl acrylate copolymers (EMA).

[0029] The structure of the present invention may be formed by any conventional process. Such processes include extrusion, coextrusion, extrusion coating, extrusion lamination, adhesive lamination and the like, and combinations of processes. The specific process or processes for making a given film which is neither oriented nor cross-linked can be selected with average skill, once the desired structure and compositions have been determined.

[0030] When the structure of the present invention is a film, the film may also be oriented either uniaxially or biaxially. Orientation can also be done by any conventional process for forming multiple layer films. A preferred process includes

the steps of coextrusion of the layers to be oriented, followed by orientation in one of the conventional processes such as blown tubular orientation or stretch orientation in the form of a continuous sheet; both being molecular orientation processes. The double bubble technique disclosure in Pahlke, U.S. Patent No. 3,456,044 is suitable for use in producing the film of this invention. The films may also be formed by a tubular water quench process. In this process the film may be extruded downwardly as a tube formed by an annular die, and carried into a water quench tank, generally with a cascade of water on the outside surface providing initial cooling. The flattened tape is withdrawn from the quench bath, is reheated (normally in a second water bath) to its orientation temperature, is stretched in the machine direction between two sets of rolls that are so rotated as to establish a linear rate differential therebetween, and is simultaneously oriented in the transverse, or cross-machine, direction as an inflated bubble trapped between the nips of the rolls. In accordance with conventional practice, the film will usually be cooled by air in the orientation zone.

[0031] The film of the present invention may also be oriented and/or cross-linked. The first step is the formation of a multiple layer film. The formation of the multiple layer film, is usually most easily accomplished by coextrusion of the desired layers. Other formation processes are acceptable so long as the resulting oriented film at the conclusion of fabrication processing is a unitary structure.

[0032] The second step is orienting the multiple layer film. One method for accomplishing orientation is by heating the film to a temperature appropriate to molecular orientation and molecularly orienting it. The film may then be optionally heat set by holding it at an elevated temperature while its dimensions are maintained. The orientation step is preferentially carried out in line with the first step, which is the film formation step of the process.

[0033] The third step is subjecting the formed and oriented multiple layer film, to electron beam irradiation.

[0034] The amount of electron beam irradiation is adjusted, depending on the make-up of the specific film to be treated and the end use requirement. While virtually any amount of irradiation will induce some cross-linking, a minimum level of at least 1.0 megarads is usually preferred in order to achieve desired levels of enhancement of the hot strength of the film and to expand the range of temperature at which satisfactory heat seals may be formed. While treatment up to about 50 megarads can be tolerated, there is usually no need to use more than 10 megarads, so this is a preferred upper level of treatment the most preferred dosage being 2 to 5 megarads.

[0035] The third step of subjecting the film to electron beam irradiation is performed only after the multiple layer film has been formed, and after molecular orientation, in those embodiments where the film is molecularly oriented. It should be noted that, in the irradiation step, all of the layers in the film are exposed simultaneously to the irradiation sources, such that irradiation of all the layers of the film takes place simultaneously.

[0036] In one embodiment of the process, the second step of orientation may be omitted and the unoriented multiple layer film may be cross-linked by irradiation treatment to produce a cross-linked, unoriented, multiple layer film.

EXAMPLES

[0037] Multilayer films may be prepared according to the present invention. Biaxially stretched three layer films may be prepared by a "double bubble" process similar to that disclosed in U.S. Patent No. 3,456,044 by coextruding the following compositions through a multilayer die, biaxially stretching the coextruded primary tube. The films may also be irradiated if desired.

EXAMPLE 1

[0038]

CEO
Tie
PVDC Copolymer
or EVOH
Tie
CEO

EXAMPLE 2

[0039]

CEO-EVA
Tie
PVDC Copolymer
or EVOH

Tie
CEO-EVA Blend

[0040] CEO is a copolymer of ethylene and an alpha olefin such as hexene-1 or octene-1 formed by the polymerisation reaction in the presence of a single site catalyst or metallocene.

[0041] The following example may also be prepared in accordance with the present invention:

EXAMPLE 3

[0042]

Meat Film - Forming Web
Formed by TWQ Process
(Tubular Water Quench Process)

LAYER 1	Nylon
LAYER 2	Tie
LAYER 3	EVOH
LAYER 4	Tie
LAYER 5	CEH or CEO

[0043] CEH is a copolymer of ethylene and Hexene-1 formed by the polymerization reaction in the presence of a single site catalyst or a metallocene. Other alpha olefins can be polymerized with the ethylene also.

Claims

1. A structure having a plurality of layers comprising:

a first layer comprising one or more polymers formed by a polymerisation reaction with a single site catalyst;
a second layer disposed adjacent to the first layer, the second layer comprising an adhesive material;
a third layer disposed adjacent to the second layer, the third layer comprising a barrier material;
a fourth layer disposed adjacent to the third layer, the fourth layer comprising a second adhesive material; and
a fifth layer disposed adjacent to the fourth layer, the fifth layer comprising a polymer formed by a polymerisation reaction with a single site catalyst or a polyamide;

wherein the first and fifth layers are outermost layers of the structure.

2. A structure according to Claim 1 wherein the single site catalyst is a metallocene.

3. A structure according to Claim 1 or Claim 2 wherein the first layer comprises a copolymer of ethylene and a C₃ - C₂₀ alpha olefin formed by a polymerisation reaction with a single site catalyst.

4. A structure according to Claim 3 wherein the alpha olefin comprises butene-1, hexene-1, 4-methyl pentene-1, or octene-1.

5. A structure according to any one of the preceding claims wherein the barrier material is selected from ethylene vinyl alcohol, polyvinylidene chloride, and metal foil.

6. A structure according to any of Claims 1 to 5 wherein the fifth layer comprises a copolymer of ethylene and a C₃ - C₂₀ alpha olefin formed by a polymerisation reaction with a single site catalyst.

7. A structure according to any of Claims 1 to 5 wherein the fifth layer comprises a blend of polymer formed by a reaction with a single site catalyst and ethylene vinyl acetate.

8. A structure according to Claim 1, wherein the fifth layer comprises a polyamide.

9. A structure according to any one of the preceding claims in the form of a thermoformable film, pouch, collapsible

tube, container or bag.

10. A structure according to any one of the preceding claims wherein the structure is formed by means of a tubular water quench process.

11. A structure according to any one of the preceding claims, wherein the first layer comprises a blend of a polymer formed by a reaction with a single site catalyst and low density polyethylene.

Patentansprüche

1. Struktur mit einer Vielzahl von Schichten, die aufweist:

eine erste Schicht, die ein Polymer oder mehrere Polymere umfasst, das bzw. die durch eine Polymerisationsreaktion mit einem "single-site"-Katalysator erzeugt wird bzw. werden,
eine zweite Schicht, die angrenzend an die erste Schicht angeordnet ist, wobei die zweite Schicht ein Klebmaterial umfasst,
eine dritte Schicht, die angrenzend an die zweite Schicht angeordnet ist, wobei die dritte Schicht ein Sperrmaterial umfasst,
eine vierte Schicht, die angrenzend an die dritte Schicht angeordnet ist, wobei die vierte Schicht ein zweites Klebmaterial umfasst, und
eine fünfte Schicht, die angrenzend an die vierte Schicht angeordnet ist, wobei die fünfte Schicht ein Polymer, das durch eine Polymerisationsreaktion mit einem "single-site"-Katalysator erzeugt wird, oder ein Polyamid umfasst,

wobei die erste und die fünfte Schicht die äußeren Schichten der Struktur sind.

2. Struktur nach Anspruch 1, wobei der "single-site"-Katalysator ein Metallocen ist.

3. Struktur nach Anspruch 1 oder Anspruch 2, wobei die erste Schicht ein Copolymer aus Ethylen und einem C₃ - C₂₀-Alpha-Olefin umfasst, das durch eine Polymerisationsreaktion mit einem "single-site"-Katalysator erzeugt wird.

4. Struktur nach Anspruch 3, wobei das Alpha-Olefin 1-Buten, 1 -Hexen, 4-Methyl-1-penten oder 1-Octen umfasst.

5. Struktur nach einem beliebigen der vorangehenden Ansprüche, wobei das Sperrmaterial aus Ethylenvinylalkohol, Polyvinylidenchlorid und Metallfolie ausgewählt ist.

6. Struktur nach einem beliebigen der Ansprüche 1 bis 5, wobei die fünfte Schicht ein Copolymer aus Ethylen und einem C₃ - C₂₀-Alpha-Olefin umfasst, das durch eine Polymerisationsreaktion mit einem "single-site"-Katalysator erzeugt wird.

7. Struktur nach einem beliebigen der Ansprüche 1 bis 5, wobei die fünfte Schicht ein Polymerblend umfasst, das durch eine Polymerisationsreaktion mit einem "single-site"-Katalysator und Ethylenvinylacetat erzeugt wird.

8. Struktur nach Anspruch 1, wobei die fünfte Schicht ein Polyamid umfasst.

9. Struktur nach einem beliebigen der vorangehenden Ansprüche in Form eines thermoformbaren Films, eines Beutels, einer zusammendrückbaren Tube, eines Behälters oder einer Tasche.

10. Struktur nach einem beliebigen der vorangehenden Ansprüche, wobei die Struktur in Form eines Schlauchs mittels eines Prozesses, der eine schnelle Abkühlung mit Wasser beinhaltet, erzeugt wird.

11. Struktur nach einem beliebigen der vorangehenden Ansprüche, wobei die erste Schicht ein Polymerblend umfasst, das durch eine Reaktion mit einem "single-site"-Katalysator und Polyethylen niedriger Dichte erzeugt wird.

Revendications

1. Structure ayant une pluralité de couches, comprenant :

- 5 une première couche comprenant un ou plusieurs polymères formés par une réaction de polymérisation avec un catalyseur à site unique ;
- une deuxième couche disposée adjacente à la première couche, la deuxième couche comprenant une matière adhésive ;
- 10 une troisième couche disposée adjacente à la deuxième couche, la troisième couche comprenant un matériau barrière ;
- une quatrième couche disposée adjacente à la troisième couche, la quatrième couche comprenant une seconde matière adhésive ; et
- 15 une cinquième couche disposée adjacente à la quatrième couche, la cinquième couche comprenant un polymère formé par une réaction de polymérisation avec un catalyseur à site unique ou un polyamide ;
- 20 dans laquelle les première et cinquième couches sont les couches les plus externes de la structure.

2. Structure selon la revendication 1, dans laquelle le catalyseur à site unique est un métallocène.

- 25 3. Structure selon la revendication 1 ou la revendication 2, dans laquelle la première couche comprend un copolymère d'éthylène et d'une alpha oléfine en C_3 à C_{20} formé par une réaction de polymérisation avec un catalyseur à site unique.

- 30 4. Structure selon la revendication 3, dans laquelle l'alpha oléfine comprend le butène-1, l'hexène-1, le 4-méthylpentène-1, ou l'octène-1.

- 35 5. Structure selon l'une quelconque des revendications précédentes, dans laquelle le matériau barrière est choisi parmi un éthylène alcool vinylique, un polychlorure de vinylidène et une feuille métallique.

- 40 6. Structure selon l'une quelconque des revendications 1 à 5, dans laquelle la cinquième couche comprend un copolymère d'éthylène et d'une alpha oléfine en C_3 à C_{20} formé par une réaction de polymérisation avec un catalyseur à site unique.

- 45 7. Structure selon l'une quelconque des revendications 1 à 5, dans laquelle la cinquième couche comprend un mélange d'un polymère formé par une réaction avec un catalyseur à site unique et d'éthylène acétate de vinyle.

- 50 8. Structure selon la revendication 1, dans laquelle la cinquième couche comprend un polyamide.

- 55 9. Structure selon l'une quelconque des revendications précédentes, sous la forme d'un film thermoformable, d'une poche, d'un tube souple, d'un récipient ou d'un sac.

10. Structure selon l'une quelconque des revendications précédentes, la structure étant formée au moyen d'un procédé d'extrusion tubulaire avec trempe à l'eau.

11. Structure selon l'une quelconque des revendications précédentes, dans laquelle la première couche comprend un mélange d'un polymère formé par une réaction avec un catalyseur à site unique et d'un polyéthylène basse densité.

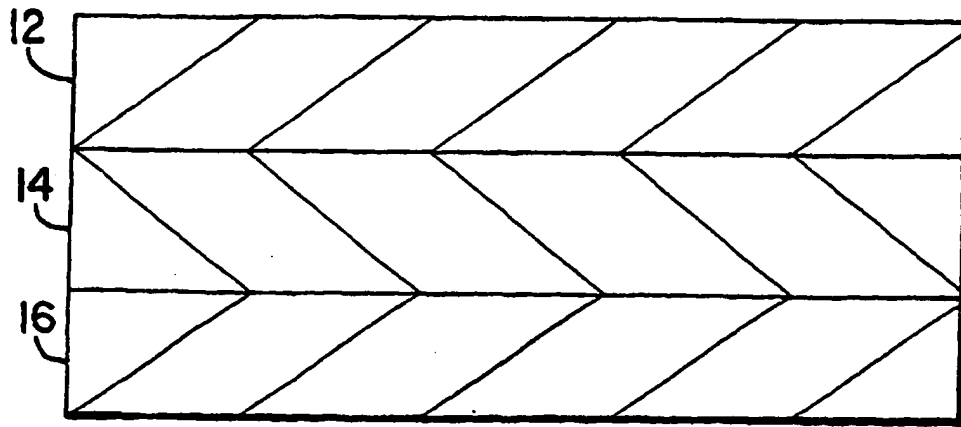


FIG. 1

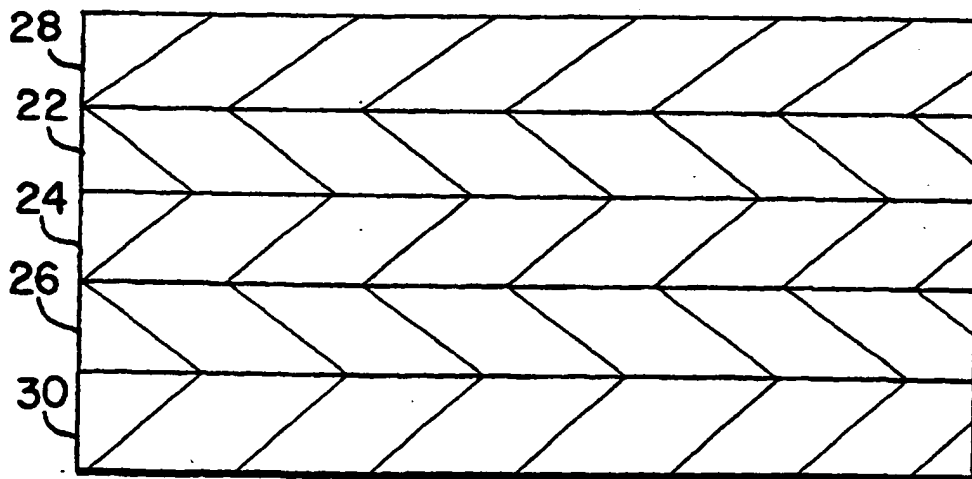


FIG. 2

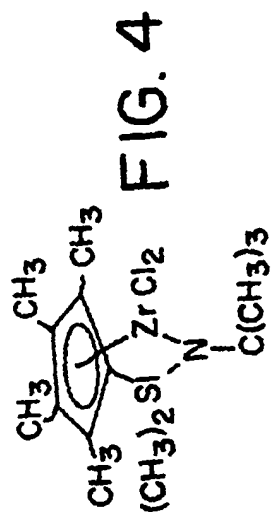


FIG. 4

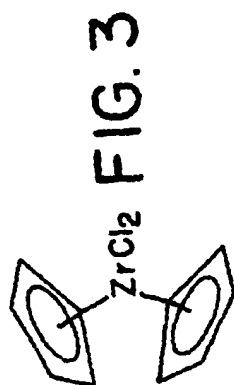


FIG. 3

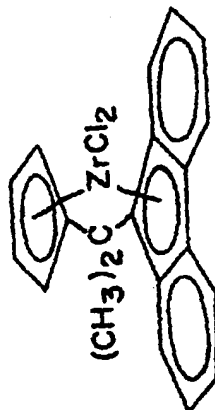


FIG. 6

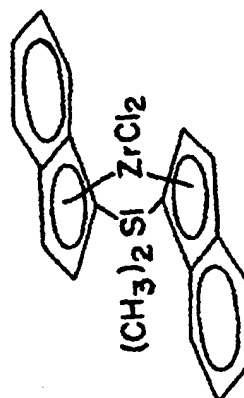


FIG. 5